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Identification of Endohedral Water in Single-Walled Carbon Nanotubes by ^{1}H NMR

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ABSTRACT

Water confinement within single-walled carbon nanotubes (SWCNTs) has been a topic of current interest, due in part to their potential nanofiltration applications. Experiments have recently validated molecular dynamics predictions of flow enhancement within these channels, although few studies have probed the detailed structure and dynamics of water in these systems. Proton nuclear magnetic resonance (^{1}H NMR) is a technique capable of providing some of these details, although care must be exercised in separating the confined water of interest from exterior water. By using controlled experiments with both sealed and opened SWCNTs and by providing a quantitative measure of water content through desorption experiments, a signature for confined water in SWCNTs has been positively identified. This endohedral or interior water is characterized by a relatively broad feature located at 0.0 ppm, shifted upfield relative to bulk water. With the identification of a signature for water inside SWCNTs, further studies aimed at probing water dynamics will be enabled.

Carbon nanotubes (CNTs) are a unique class of materials with a host of novel thermal, mechanical, and electrical properties and applications. These materials also have potential as nanofluidic conduits. Molecular simulations[1] and recent experiments[2,3] suggest significant enhancements in gas transport through CNT channels. More recent work has focused on the unique water transport characteristics of single-walled CNTs (SWCNTs), given their similarities to biological channels that can efficiently shuttle water through cell membranes. The majority of the studies to-date have been molecular simulations.[4–9] Unique properties not observed in bulk water have been predicted, such as a low temperature water phase that consists of an “ice-nanotube”, comprising of 6- or 7-membered water rings.[4] Another novel effect consists of frictionless, pulsed one-dimensional transport of water,[10] with rates of up to 30 water molecules per nanosecond, comparable to water transport in the transmembrane protein aquaporin.[11] Experimental studies have now corroborated some of the enhanced water[2,12] and gas[1,3] transport predictions. These studies compared flow rates and flow velocities to the simulations, and indicated orders of magnitude faster transport than predictions of continuum, hydrodynamic theory. However, for a comprehensive understanding of the water transport inside carbon nanotubes, a better understanding of the microscopic properties of water under these experimental conditions is needed. For example, it remains an open question whether the observed flow enhancement is a consequence of confinement-induced ordering or the unique surface properties (i.e., atomic smoothness and hydrophobicity) of the SWCNTs.

^{1}H nuclear magnetic resonance (NMR) is a technique that offers unique advantages in studying the properties of water under nanoscale confinement. The much larger transverse (spin−spin) relaxation time of mobile water compared with solid ice (~6 μs) can be used to monitor the process of freezing, as reported in an earlier study.[13] In that study, a feature that emerges upfield, or at lower parts per million relative to bulk water, was attributed to water inside SWCNTs.[13] Complementary to studies by molecular dynamics simulations,[9,14] NMR-observed water adsorption isotherms were used to quantify the amount of H_2O adsorbed inside SWCNTs.[15] It was observed that the confined water inside SWCNTs exhibits significantly shorter transverse relaxation times than bulk water,[15] similar to that of water confined in nanopores of activated carbons.[16] The water adsorption isotherm indicates that the adsorbed water content

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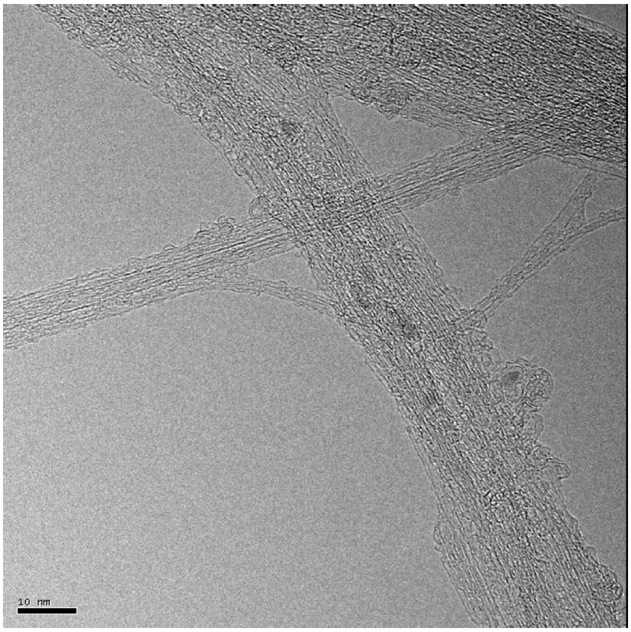

Figure 1. TEM micrograph of the HiPCO SWCNTs used in this study. The average diameter is approximately 1 nm.

in SWCNTs is about 3 mmol/g or 5.4 g of water per 100 g SWCNTs, which corresponds to about a 20% occupancy of the available inner volume of 1.4 nm diameter SWCNTs.[15] This low water occupancy could be attributed to the fact that the SWCNT sample used in the NMR isotherm study is highly defective due to the aggressive chemical treatment with strong acids used in cutting the tubes. Other NMR studies[17,18] revealed the coexistence of water with different mobility absorbed in SWCNTs by examining the temperature dependence of the ^{1}H and ^{2}H NMR line width. A study[19] using ^{1}H magic-angle-spinning (MAS) NMR achieved enhanced spectral resolution to resolve two peaks with distinct chemical shifts for water absorbed in SWCNTs. The two peaks were attributed to water in the interior and exterior of the tubes, albeit at anomalously large water content inside the tubes ranging from 37 to 367 wt % (2.1−20.4 mmol of water per gram of SWCNTs). These results indicate that, while ^{1}H NMR is potentially a very versatile method for probing confined water inside SWCNTs, further identification of water inside SWCNTs by ^{1}H NMR is needed.

In this communication, we describe a carefully controlled study of water adsorption by SWCNTs, with the primary aim of providing an unambiguous ^{1}H NMR signature for water trapped inside SWCNTs. High-speed MAS conditions (20 kHz) were used here, as compared with the prior study,[19] in order to increase spectral resolution. We look at both closed and uncapped SWCNTs, paying particular attention to the proton background, a potentially significant interference in spectral interpretation.

For these studies, we utilize HiPCO SWCNTs (Carbon Nanotechnologies, Inc.) of high purity (SP-SWNT, $<$ 5 wt % impurities) to reduce the influence of competing water adsorption sites and effects of magnetic particles. Transmission electron microscopy (TEM) analysis (see Figure 1) confirms an average diameter of 1 nm, as reported by the vendor. All samples analyzed are packed under ambient conditions and initially stored in a desiccator to remove background water. For water uptake experiments, liquid water is added to the top of the packed SWCNTs sample using a microliter-calibrated syringe; the quantity of water added is reported as a weight percentage relative to the mass of the packed SWCNT sample. The ^{1}H spectrum (see Supporting Information for more detail on the NMR measurement conditions) is measured immediately after the addition of this water, and the sample is then placed back into the desiccator to desorb excess water from it. ^{1}H NMR spectra are then remeasured at regular time intervals to monitor the desorption process.

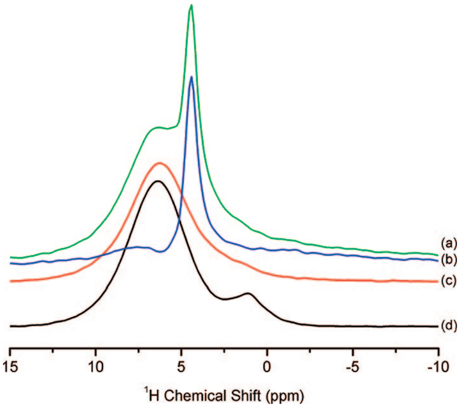

Figure 2. ^{1}H NMR spectra of (a) water absorbed by sealed HiPCO SWCNTs, (b) background correction of (a), (c) dry SWCNTs, and (d) the empty NMR MAS rotor in the probehead.

The electrical conductivity of SWCNTs can often present a problem with respect to tuning of the NMR probe, as seen in the change in the probe's Q-factor, which is defined as the ratio of ^{1}H Lamor frequency to the width of the tuning curve at −3 dB from its baseline. When the probe with an empty MAS sample holder (rotor) is well-tuned and matched, the Q-factor is about 320, while it is lowered to 110−130 when loaded with a SWCNT sample. As seen in Figure 2, even after a Q-factor correction, the proton signal from the empty rotor (Figure 2d) is noticeably different from that of the rotor packed with SWCNTs (Figure 2c). Thus, background subtraction that only considers the Q-factor difference would be unreliable in studying water adsorption by SWCNTs, either qualitatively or quantitatively. This subtraction method might work if factors such as the pulse length and power strength were accounted. However, as we are only concerned with interrogating the absorbed water in the samples and not other sources of protons, all spectra associated with water treated SWCNTs are referenced to those obtained before adding liquid water (the "dry" spectrum). The effectiveness of this method of subtracting the "dry" background can be seen by comparing Figure 2a,b, before and after subtracting the "dry" background from the SWCNTs dosed with about 100 wt % water.

It has been reported that high-temperature vacuum-annealing (800 °C at 5×10^{-6} Torr for 1 h) is effective in capping or sealing the open-ended SWCNTs.[20] The ^{1}H NMR spectrum of the annealing-sealed SWCNTs dosed with water

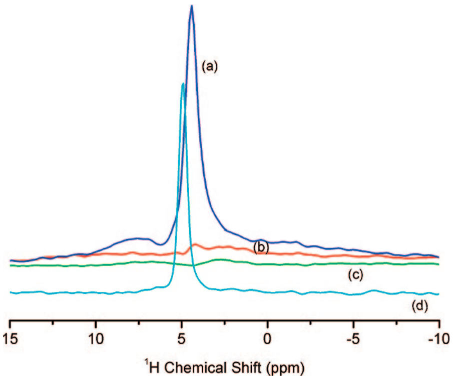

Figure 3. ^{1}H NMR spectra of water absorbed by sealed HiPCO SWCNTs with (a) 100 wt % water, (b) 40 wt % water, (c) 10 h desiccator drying of (a). As a comparison, the spectrum of liquid water (d) is also shown.

is a crucial control sample to ascertain the signature of water that is exterior to the SWCNTs. Figure 3 compares the ^{1}H NMR spectra of samples with different amounts of water added. There is only a single peak centered at around 4.4 ppm when 100 wt % water was added and the water is totally desorbed from the sample in about 10 h; see Figure 3c. This water peak is close to the bulk water chemical shift (4.9 ppm, Figure 3d), and shows only slight broadening. When less water is added (40 wt %, Figure 3b), the spectrum is a broad hump centered around 2−3 ppm, which may arise from water adsorbed on defects and impurities such as amorphous carbon-coated metal catalyst particles. Thus, only bulk-like water is observed for the sealed SWCNTs when approximately 100 wt % water is added. It should be noted that the big hump centered at 7.5 ppm is likely an artifact from the background correction.

The sealed SWCNTs were subsequently opened by controlled oxidation through thermogravimetric analysis (TGA) at 350 °C in ambient air. Previous studies[17] have indicated that this treatment is sufficient to uncap the CNTs, proceeding sequentially from the ends of the tubes where defect sites are created. Less than 10% total weight loss was observed from the sample after this oxidation treatment (see Supporting Information). After opening, 146 wt % of water was added to the sample and ^{1}H NMR spectra were acquired as a function of desiccation time (see Figure 4). The desorption experiment reveals that there are two principal proton peaks associated with the sample (i.e., two differently adsorbed water molecules) resonating at 4.3 ppm and 0 ppm, where the broad hump centered around 2−3 ppm that appears after 4 h of desorption may again be associated with water adsorbed on defects and impurities. Since this broad hump is present in both sealed and opened samples, the amount of water associated with this broad feature (corresponding to about 30 wt %) is excluded below from the quantitative analysis of the endohedral adsorption of water. The earlier study by Sekhaneh et al.[19] indicates that the effect of higher concentrations of catalyst in CNT samples is to cause inhomogeneous broadening of the water resonance line, producing spinning sidebands under MAS conditions. We observe no such effects in these spectra, providing confirmation that the impurity level of the sample is acceptably low.

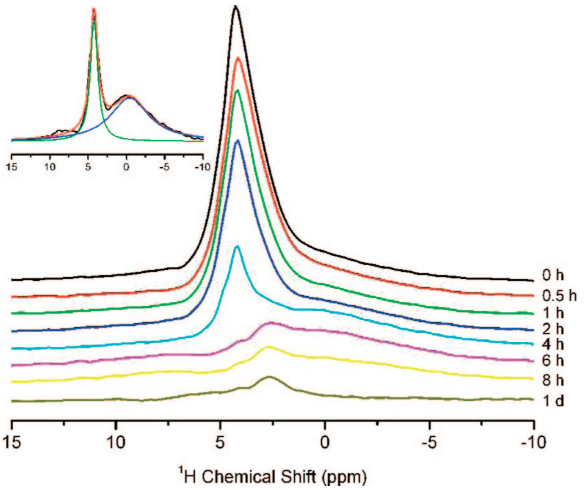

Figure 4. ^{1}H NMR spectra of water desorption from HiPCO SWCNTs that were first annealed at 800 °C, then opened via TGA in air; inset: deconvolution of the spectrum after 4.0 h desorption, subtracting out the contribution after 1 day of desorption.

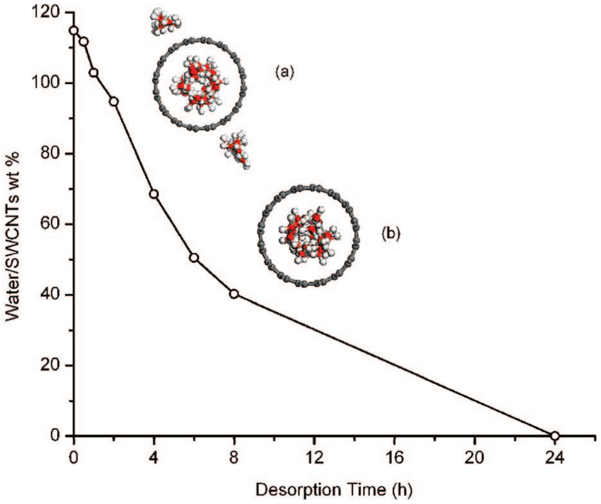

Figure 5. The desorption curve of water from HiPCO SWCNTs. Insets are illustrations of water absorption by SWCNTs, (a) inside and outside SWCNTs, and (b) inside SWCNTs only.

By comparing these spectra and the desorption behavior to that of the sealed SWCNTs (Figure 3), it becomes clear that the peak at 4.3 ppm is associated with water outside of the SWCNTs and that the broad hump centered at 0 ppm is from endohedral or interior water of the SWCNTs. After 4 h of desorption, most of the water resonating at 4.3 ppm is lost, and the total water content is lowered to 70 wt % (Figure 5). After 6 h, the free water is completely desorbed, as no obvious peak at 4.3 ppm is observed experimentally, and the water molecules associated with the broad 0 ppm peak start to desorb. After about 24 h desorption, only the peak at 2.5 ppm is observed, and the water associated with that peak is approximately 30 wt %, comparable in area to the feature in the spectrum of the sealed SWCNTs for which 40 wt % of water was added (see Figure 3b). The deconvolution of the spectrum at 4 h, subtracting out the spectrum after 1 day (see inset of Figure 4), reveals that the relative areas are about 1:2 under the 4.3 ppm and 0 ppm peak, respectively. In other words, there is about 47 wt % water associated with the 0 ppm endohedral water feature, which is comparable to the amount of endohedral water after 8 h of drying (40 wt %). The HiPCO SWCNT sample, with diameters of ~1.0 nm, corresponds roughly to an (8, 8) SWCNT in size (1.08 nm diameter). By accounting for the nominal diameter of the carbon atom (~0.34 nm)[9] and by assuming that water fills the entire tube volume, except for the space 0.17 nm from the nanotube wall, the water filling ratio is about 16.6 wt % (or 9.3 mmol/g if we take the average density of filled water as 1.0 g/mL). The experimentally observed filling ratio is approximately 3 times this value and is higher than that predicted by molecular dynamics simulations[9] and saturation absorption measurements.[14] This discrepancy is most likely due to the accuracy of the syringe, neglecting water loss during initial sample packing, and artifacts associated with the background correction. Nevertheless, we contend this 0 ppm peak is associated with water adsorbed inside SWCNTs for two primary reasons: (1) the relative desorption behavior, where the 4.3 ppm exterior water desorbs before that at 0.0 ppm, and (2) the broad 0 ppm feature is only observed for tubes opened by TGA and not for sealed tubes.

In addition to careful quantification of the amount of water that can occupy the nanotube pores, the chemical shift of this endohedral water is another key piece of information needed for spectral interpretation. It was previously predicted that the induced ring current effect for an (8, 8) SWCNT results in an upfield shift of about 5−5.5 ppm (relative to bulk water) for endohedral water 2−3 Å from the SWCNT wall, while a shift of only 0.5 ppm downfield results for exterior water 2−3 Å from the wall.[19] Indeed, the experimentally observed chemical shift for water inside a similarly sized SWCNT in the present study agrees with these model predictions, and interestingly, a molecular dynamics simulation[9] predicts that only a monolayer of water can be accommodated within an (8, 8) SWCNT.

In summary, to use ^{1}H NMR as a tool to study confined water in CNTs requires careful quantification of the total water dosage of the sample, careful consideration of the relative chemical shifts of various features in the spectra, and careful background subtraction in order to eliminate nonwater related features in the spectra. The present study has provided strong evidence for the assignment of a broad feature at 0.0 ppm to that of water occupying the endohedral of SWCNTs. With this knowledge, dynamic experiments aimed at interrogating this confined water can be carried out and may provide insight into the origin of the flow enhancement observed through CNT channels.

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Supporting Information Available: Oxidative opening of HiPCO SWCNTs and detailed ^{1}H NMR sample preparation and data collection. This material is available free of charge via the Internet at http://pubs.acs.org.

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